

PATENT SPECIFICATION

1,120,147

DRAWINGS ATTACHED.

The Inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949, are DRAHOSLAV LIM, of No. 8 V. Huga, Prague 5, Czechoslovakia, JIRI COUPEK, of No. 5 Zavadilova, Prague 6, Czechoslovakia, JIRI BACA, of No. 2 Jakubska, Prague 1, Czechoslovakia, LUBOMIR LOCHMANN, No. 22 Severni, Prague 4, Czechoslovakia, KAREL JUZI, of No. 5 Kourimska, Prague 3, Czechoslovakia, all Czechoslovakian citizens.

1,120,147



Date of Application and filing Complete Specification:
28 June, 1966. No. 28921/66.

Application made in Czechoslovakia (No. 4327) on 6 July, 1965.

Complete Specification Published: 17 July, 1968.

© Crown Copyright 1968.

Index at Acceptance:—C3 P(8D2A, 8D2B2, 8D3A, 8P1B, 8P3, 8P6G, 8P6X, 13D3, 13G2A, 13G4A, 13G5, 13H1, 13H2A, 13H3, 13T1A, 13Y).

Int. Cl.:—C 08 f 1/28.

COMPLETE SPECIFICATION.

A Method of Preparing Polymers by Means of Anionic Initiators.

- We, CESKOSLOVENSKA AKADEMIE VED, a Czechoslovakian body corporate, of No. 3 Narodni, Prague 1, Czechoslovakia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a method of preparing polymers by means of anionic initiators. The polymerisation process by which polymers are prepared from monomers is chosen according to technological requirements and also to properties of the polymer required. It is known that a number of polymers, for example those of the acrylic type, are formed very easily by anionic polymerisation, but radical polymerisation is for example more convenient for work on a larger scale.
- The reason anionic polymerisations are little used is because of the strongly exothermic course of the reaction and the high cost of the initiator. The activation energy is low and therefore temperature has only a small effect on the polymerisation, in contradistinction to radical polymerisation wherein the determining factor is the decomposition of the initiator.
- In laboratory studies of anionic polymerisation, if the reaction is to be investigated, it is necessary to work with dilute solutions or dispersions and at low temperature.
- Most of the data on anionic polymerisation of the above monomers have thus been obtained. Polymerisation is a complex of many competitive and consecutive reactions and the usual control of the reaction determines only the final state of the polymer. An example of such a difficulty controllable polymerisation is that of methyl methacrylate by means of Grignard reagents or organometals of alkaline metals.
- It has been shown that suitable initiators for the polymerisation of acrylates, methacrylates and nitriles are alcoholates of lithium and alkaline metals. Initiation is slowed down and thus a mild, controllable course of polymerisation is accomplished, without the necessity of working in high dilutions of monomer or at very low temperatures.
- The rates of reaction with tert. alcoholates of alkaline metals are different. In the polymerisation of methacrylates, lithium alcoholate acts most slowly. The use of sodium alcoholate increases the polymerisation rate of the monomers. It is usually possible to observe acceleration in the polymerisation. Potassium tert. alcoholate, of the readily available tert. alcoholates of alkaline metals, acts most rapidly. Polymerisation with the addition of these alcoholates is almost as rapid as with alkyl metals.
- There is no significant difference in the

[Price 4s. 6d.]

rate of initiation of acrylates between the various alcoholates. The polymerisation is characterised by very rapid reaction.

Accordingly the present invention is a method for the preparation of polymers by means of anionic initiators or catalysts, using monomers which rapidly polymerise with these initiators or catalysts and wherein termination occurs, characterised in that the anionic initiators or catalysts of polymerisation are added portionwise into a stirred polymerising mixture throughout the course of the reaction and wherein such additions are only effected when the temperature of the reactants falls below that temperature at which the effectiveness of the initiator or catalyst is decreased to one half in 15 minutes or less under the conditions of the reaction.

According to the invention, to a monomer maintained at a certain temperature is added an initiator or catalyst, the major part of which, in a fraction of a second to several minutes, has participated and has been consumed in the reaction with the monomer. Polymerisation manifests itself by increased temperature. The whole process is controlled by relating addition of initiator or catalyst to temperature. Thus, after setting a certain upper temperature limit for the reaction, addition of initiator to monomer is only effected at times when the reaction mass is below the temperature limit. At temperatures above the limit, no initiator or catalyst is added. The process may be automated so that no additions are made by a dispensing device when the limiting temperature is exceeded, using an electrical system similar to a thermostat controlled system.

Polymerisation can thus be carried out substantially isothermally i.e. with temperature fluctuation within the range of several tenths of, to several degrees, C. In principle, all ionic polymerisations with rapid initiation in which termination occurs can be carried out according to the process of the invention. The process is especially suitable for the system: organometals and acrylates ethacrylates or nitriles; tert. alcoholates of lithium, sodium or potassium and acrylates; tert. alcoholates of sodium, potassium and methacrylates or nitriles.

The advantage of the process according to the invention is that even when using an undiluted monomer i.e. polymerising the monomer in bulk, it is possible to polymerise at room temperature or above, up to about the boiling point of the monomer. The molecular structure of the polymer changes with temperature so that the structure may conveniently be controlled in this way. Also the stereoregularity of the polymer depends on temperature. Since the velocity of polymerisation and its course are

smoothly controlled by the addition of the catalyst at below a specified temperature, loss of control of the reaction is impossible; (the course is practically isothermal). It is possible by changing the temperature limit and selecting a suitable anionic catalyst to change the properties of the polymer over a wide range.

EXAMPLE 1

The drawing represents schematically the arrangement of the experiments according to this invention. A three-necked glass reactor was provided with a ground glass stirrer sealed with mercury 14, 15. One of the side necks was closed by a special pressure closure 10 sealed with acrylonitrile rubber permitting the dosage of the initiation solution by means of a syringe 7. The other neck is terminated by a three-way cock 8. The reactor is further provided with a side tube 11 serving as a holder for a thermocouple (copper-constantan) battery.

The reaction vessel was filled with a monomer in an inert atmosphere of dry nitrogen freed from oxygen by a contact catalyst. The monomer in the reactor was freed from oxygen by repeated evacuation and flushing with nitrogen at the boiling point of nitrogen at 10^{-6} mm Hg. with final heating to room temperature in nitrogen. The reactor was then immersed in a thermostated bath 12 and its content was brought to the temperature of the experiment with a constant rate of stirring.

A solution of an initiator in an inert solvent (linear saturated hydrocarbons, aromatic hydrocarbons, etc.) was placed in the syringe 7 of the dosing device 6, which syringe was protected against the intrusion of air, oxygen and moisture. The polymerisation began by starting the addition of initiator from dosing device 6 controlled by an impulse compensation controller 3. The reaction heat of the polymerisation is conducted away by the walls of the reactor to the environment. In view of the rapid termination reaction, the rate of polymerisation and thus also the amount of heat produced is proportional to the rate of dosage. The dosing device is controlled by the temperature of the polymerising mixture. The difference between the temperature in the reactor and that of the thermostatically controlled bath is a measure of the rate of polymerisation. At a steady state the heat conducted away to the environment is compensated by the polymerisation heat of the reaction controlled only by the amount of the solution of the initiator added into the mixture. The steady state is reached within several minutes of the starting of the dosing device. The amount of initiator added is dependent on the departure of the actual temperature of the polymerising mix-

ture from the set temperature limit and when this limit is reached or exceeded, the addition of the initiator is interrupted. The initiator is quickly consumed in the system, the rate of polymerisation decreases and the temperature of the mixture again drops below the set limit. At this moment the automatic control again switches in the dosage device. The polymerisation thus takes place at a constant temperature with temperature variations a maximum of 0.2°C. The course of the temperature of the polymerising mixture and the amount of the catalyst supplied are recorded throughout the experiment. Knowing the calorimetric constants of the system it is thus possible to calculate the exact instantaneous value of the conversion of monomer to polymer.

In this example, 100 parts of methyl methacrylate were polymerised at 20°C. Used as initiator were 0.047 parts of tert. butyl lithium dissolved in 4.7 parts of dried benzene. After a 32% conversion was reached, the addition of the initiator was interrupted and the polymerisation mixture was stirred for 15 more minutes. After addition of 0.1 part of acetic acid the resulting polymer/monomer mixture of methyl methacrylate may be used for further processing.

EXAMPLE 2

Into the polymerisation reactor according to Example 1 was weighed 100 parts of methyl methacrylate and, after elimination of oxygen and adjusting the temperature to 20°C., 0.0075 parts of potassium tert.-butyl alcoholate in 2 parts of benzene was added by the dosing device. The polymerisation occurred and was controlled by further additions of catalyst for a period of 1 hour. The resulting polymer after precipitation in hexane and washing was dried. The yield amounted to 21%.

EXAMPLE 3

In the polymerisation device according to Example 1, 100 parts of methyl methacrylate at 20°C were polymerised. During 1 hour, 0.027 parts of triphenylmethyl-sodium dissolved in 6 parts of benzene and 2 parts of tetrahydrofuran were added dosage wise, only when the temperature did not exceed 20°C. The deep red solution of the initiator is immediately decolourised in contact with the monomer. After precipitation and drying of the polymer, 20 parts of a colourless product were obtained.

EXAMPLE 4

100 parts of dry n-butyl methacrylate were weighed into the reactor and after bringing to 20°C, 0.008 parts of tert.-butyl lithium in 0.9 parts of benzene were added by the controlling device, then the dosage

was interrupted due to rise of temperature. The reaction mixture was stirred for a period of 15 minutes until the temperature of the mixture became equal to that of the bath (20°C). Further polymerisation was initiated by addition of 0.006 parts of sodium tert.butyl alcoholate in 4.5 parts of benzene. After 1 hour a 15% conversion of monomer to polymer was reached.

EXAMPLE 5

Into the polymerisation reactor according to Example 1 was weighed 100 parts of dried and distilled methyl acrylate, polymerisation was carried out at 20°C by controlled additions of 0.198 parts of lithium tert.-butyl alcoholate in 9 parts of benzene, by the apparatus previously described. After 30 minutes a 5% conversion was reached.

EXAMPLE 6

In the device according to Example 1, 100 parts of n-butyl acrylate was polymerised at 20°C under the initiation of controlled additions of 0.034 parts of sodium tert.-butyl alcoholate in 5 parts of benzene. At a temperature difference of 0.5°C between the reactor and the environment, a 15% conversion was reached in 1 hour.

EXAMPLE 7

100 parts of acrylonitrile were polymerised at 20°C under the initiation of controlled additions of a total of 0.009 parts of sodium tert.-butyl alcoholate in 6 parts of benzene. The solution of the initiator was added over a period of 45 minutes. The resulting polymer (35 parts) was freed from monomer by filtration, washed and dried.

This type of precipitation polymerisation may easily be effected continuously so that the polymer is continuously or batchwise separated and the consumed monomer is replenished.

WHAT WE CLAIM IS:—

1. A method for the preparation of polymers by means of anionic initiators or catalysts, using monomers which rapidly polymerise with these initiators, or catalysts, and wherein termination occurs, characterised in that the anionic initiators or catalysts of polymerisation are added portionwise into a stirred polymerising mixture throughout the course of reaction and wherein such additions are only effected when the temperature of the reactants falls below that temperature at which the effectiveness of the initiator or catalyst is decreased to one half in 15 minutes or less under the conditions of the reaction.

2. A method according to Claim 1, characterised in that a monomer is used in the absence of solvents or diluents and the polymerisation is stopped after reaching a

conversion corresponding to the desired concentration of dissolved polymer in monomer.

3. A method according to Claim 1, characterised in that monomer is used in the absence of solvents or diluents and an insoluble polymer is continuously separated.

4. A method according to any one of Claims 1 to 3, characterised in that the controlled polymerisation is carried out at a temperature of from -30° to $+80^{\circ}\text{C}$, preferably at room temperature.

5. A method of preparing polymers in

accordance with Claim 1 by means of anionic initiators or catalysts according to any of the Examples.

6. Polymers whenever prepared by the method of any one of Claims 1 to 5.

H. D. FITZPATRICK & CO.,
Chartered Patent Agents,
5 Park Gardens,
Glasgow, C.3,
and
27 Chancery Lane,
London, W.C.2.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1968.
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.

1120147 COMPLETE SPECIFICATION
1 SHEET This drawing is a reproduction of
the Original on a reduced scale

